

AUTHOR: Vol'kenshteyn, F.F. (Wolkenstein, F.F.)

TITLE: On the Problems of Semiconductor Theory in Connection with the Catalysis Theory (O zadachakh, stoyashchikh pered teoriyey poluprovodnikov v svyazi s problemoy kataliza)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Vol. XXI, #2, pp 176-178 1957, USSR, Seriya fizicheskaya

ABSTRACT: The surface of a semiconductor possesses a specific property to catalyze many chemical reactions. The phenomenon is reduced to the following process: molecules of reacting gases are absorbed on the surface of a semiconductor, then being in the absorbed state react with each other, and the reaction products are desorbed again. Thus the reaction is transferred from the gas phase to the semiconductor surface. The problem is why this leads to its substantial acceleration (sometimes in tens of thousands of times)?

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The other problems awaiting their theoretical clarification are as follows:

1. The mechanism of catalytic property of a semiconductor is hidden within the semiconductor itself. The problem is to discover this mechanism.
2. Adsorption in question is a so-called "khemosorbtsiya", chemical adsorption, caused by the forces of chemical nature. What is the mechanism of the chemical adsorption, that is the mechanism of forming a chemical connection between a crystal and a gas molecule?
3. What is the origin of the potential barrier on the adsorption curve, the origin of the activation energy?
4. Molecules are often dissociated during the chemical adsorption. What is the mechanism of this dissociation?

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5. The catalytic activity of a semiconductor essentially depends on the character and concentration of admixtures contained within its volume. By what a way do admixtures so considerably affect chemical processes taking place on the semiconductor surface?

6. Why is the activity of a semiconductor connected with the concentration of free electrons and holes contained in it?

These problems have been the subject of theoretical investigations in the Catalysis Laboratories of the Institute of Physical Chemistry. No references are cited.

INSTITUTION:

Institute of Physical Chemistry of the USSR Academy of Sciences

PRESENTED BY:

SUBMITTED: No date

AVAILABLE: At the Library of Congress

Card 3/3

AUTHOR: Vol'kenshteyn, F.F. (Wolkenstein, F.F.)

TITLE: On Some Problems of Semiconductor Catalysis (O nekoto-rykh voprosakh poluprovodnikovogo kataliza)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Vol XXI, #2, pp 179-182 1957, USSR, Seriya fizicheskaya

ABSTRACT: There are experimental facts which indicate a close correlation between electronic properties of a semiconductor and its catalytic and adsorption qualities. Chemical adsorption results in charging the surface of a semiconductor. Therefore, energetic zones are being curved at the surface and the contact potential and electric conductivity of a semiconductor can change. These changes following adsorption have been actually observed by V. Lyashenko and I. Stepko.

The probability for a chemically adsorbed molecule to be in a neutral or charged state depends on the level of the chemical potential or the concentration of free electrons and holes in the crystal.

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TITLE:

On Some Problems of Semiconductor Catalysis (O nekotorykh voprosakh poluprovodnikovogo kataliza)

The dependence of the adsorption activity of mercury sulfide on its stoichiometric composition and the effect of lighting on the adsorption activity point out in this direction. Sometimes, however, the lighting leads to an opposite effect, i.e. decrease of the adsorption activity, as Terenin and Myasnikov experiments showed.

Another group of facts is concerned with effects of admixtures on the semiconductor catalytic activity. The latter is characterized by the constant of rate K which usually satisfy Arrhenius' law:

$$K = K_0 e^{-E/KT}$$

where E is activation energy and T is temperature.

The insertion of an admixture into a semiconductor leads to the change of both activation energy E and pre-exponential multiplier K_0 .

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TITLE:

On Some Problems of Semiconductor Catalysis (O Nekotorykh voprosakh poluprovodnikovogo kataliza)

Reaction of ethylene oxidation on catalyzer $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ with admixture of Na_2SO_3 studied by Krylov and Margolis showed that one and the same admixture, and used in the same quantity, expedites the reaction at low temperatures and dopes the catalyzer, i.e., inhibits the reaction at high temperatures. Depending on its concentration, one and the same admixture, at the same temperature, can either promote a reaction or inhibit it.

In the author's opinion, the insertion of admixtures changes the concentration of the electronic and hole gas in a semiconductor. This concentration determines the reaction activity of the molecules adsorbed on the semiconductor surface and catalytic activity of the molecules.

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Theories used at present are of a phenomenological

TITLE: On Some Problems of Semiconductor Catalysis (O Nekoto-
rykh voprosakh poluprovodnikovogo kataliza)
character. The future theory, the electronic catalysis
theory, is in the beginning phase of its origination.
The article contains 4 graphs. No references are
given.

INSTITUTION: Institute of Physical Chemistry of the USSR Academy of
Sciences

PRESENTED BY:

SUBMITTED: No date

AVAILABLE: At the Library of Congress

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Vol'kenshteyn, F.F.

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topo-
chemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3891.

Author : F.F. Vol'kenshteyn.

Inst :

Title : Some Questions Concerning Semiconductor Catalysis (According
to Materials of International Catalysis Congress at Philadel-
phia).

Orig Pub: Uspekhi khimii, 1957, 26, No 6, 659-672.

Abstract: No abstract.

Card : 1/1

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VOLKENSHTEYN, Fedor F. (Moscow)

"Towards the Electron Theory of Chemical Absorption in Semi-Conductors,"
(Plenary lecture).

report submitted for Annual Meeting East German Chemical Society, 28 Oct -
1 Nov 1958, Leipzig, G.D.R.

VOL'KENSHTEYN, F.F.

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PHASE I BOOK EXPLOITATION

SOV/1285

Akademiya nauk Belorusskoy SSR. Institut khimii

Sbornik nauchnykh rabot, vyp. 6 (Collection of Scientific Works of the Institute of Chemistry, Belorussian SSR Academy of Sciences, N. 6) Minsk, Izd-vo AN Belorusskoy SSR, 1958. 271 p. 1,100 copies printed.

Ed.: Yerofeyev, B.V., Academician, BSSR Academy of Sciences; Tech. Ed.: Volokhanovich, I.

PURPOSE: The book is intended for chemists engaged in research in specialized fields.

COVERAGE: The book is a collection of scientific articles dealing with varied subjects, such as problems in electron theory of semiconductors, catalysis, autoxidation of abietic acid, thermodynamics of some reactions of sulfur organic compounds and reactions of alkyl, aryl, acyl-oxy radicals in the liquid phase. Personalities are mentioned in the individual articles. There are 331 references, of which 215 are Soviet, 75 English, 30 German, 10 French, and 1 Finnish

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Collection of Scientific Works (Cont.)

SOV/1285

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VOL'KENSHTEYN, F.F.

SOV/30-58-7-34/49

AUTHOR: Krylov, O. V., Candidate of Chemical Sciences

TITLE: Physics and Physical Chemistry of Catalysis (Fizika i fiziko-khimiya kataliza) Transactions of the All-Union Conference (Vsesoyuznaya konferentsiya)

PERIODICAL: Vestnik Akademii nauk SSSR, 1958, Nr 7, pp. 119 - 122 (USSR)

ABSTRACT: This conference convened in Moscow between March 20th and March 23rd. It was called by the Department of Chemical Sciences and the Institute of Physical Chemistry of the AS USSR (Otdeleniye khimicheskikh nauk i Institut fizicheskoy khimii Akademii nauk SSSR). It was attended by more than 600 persons from different towns of the Soviet Union as well as from countries of the people's democracies. Nearly 100 reports were submitted, 78 of which were given to the participants for discussion. The remainder was read. The following reports were heard:

1) S. Z. Roginskiy, (Institute of Physical Chemistry, AS USSR), spoke about the selective methods concerning semiconductor catalysis.

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- 2) V. V. Boldyrev, Tomsk University, used electron representations for the explanation of the course of topochemical reactions.
- 3) N. P. Keyyer, (Institute of Physical Chemistry, AS USSR), used electron representations for the clarification of the characteristics of heterogeneity of the active surface of semiconductor contacts.
- 4) F. F. Vol'kenshteyn, V. B. Sandomirskiy and Sh. M. Kogan, (Institute of Physical Chemistry, AS USSR), investigated the influence of exposure as well as of an external electric field on the absorptive power of a semiconductor.
- 5) A. N. Terenin spoke about the investigation of the structure and the behavior of surface formations in the case of adsorption and catalysis.
- 6) V. F. Kiselev (Moscow University), dealt with problems concerning the elementary act of catalysis.
- 7) G. K. Boreskov, Physical-Chemical Institute imeni L. Ya. Karpov (Fiziko-khimicheskiy institut im. L. Ya. Karpova), reported on the dependence of the catalytic activity of metals on their position in the periodic system of elements.

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AUTHOR: Vol'kenshteyn, F.F. (Moscow) SOV/74-27-11-2/5

TITLE: Present State of the Electron Theory of Catalysis on Semiconductors (Sovremennoye sostoyaniye elektronnoy teorii kataliza na poluprovodnikakh)

PERIODICAL: Uspekhi khimii, 1958, Vol 27, Nr 11, pp 1304-1320 (USSR)

ABSTRACT: A short summary of the results of a series of new theoretical publications in this field is given. One of the main problems treated is: What is the importance of the electron theory in catalysis on semiconductors. The electron theory first explains the adsorption and desorption mechanisms. The particles adsorbed at the surface are regarded as structural defects of the surface. Experiment carried out by the author in 1948 (Ref 1). The adsorbed particle enters the adsorbing lattice and participates in the electron household of the lattice. Two forms can be distinguished in the formations on the surface: 1) The "weak" chemisorption, particles and centre of adsorption are a whole, the particle remains electrically neutral. 2) "Solid" chemisorption, the adsorbed particle has a free electron (donor) or an electronic vacancy (acceptor). The two latter bonds may be of purely ionic or purely homeopolar or also of mixed nature according

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Present State of the ~~Electron Theory~~ of
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to the nature of the adsorbent, and the adsorbate. The chemically adsorbed particles i.e. the "solid" ones meet with other chemisorbed particles or particles from the air and may enter in reaction with them. Their appearance on the surface is responsible of the catalytic process. The "weak" binding is based on the concept of a couple of free valencies migrating on the surface. The removal of one of the 2 bindings leads to a "solid" acceptor or donor binding. All transitions from one type of binding into the other are possible. The probability that a certain number of particles is in one of these bindings is influenced by the position of the Fermi level. The Fermi level is the length of the distance between the zone of valencies and the zone of conductivity in the semiconductor. The position of the Fermi level thus defines the reaction velocity (the Fermi level enters the energy of activation as term of a sum). Boreskov and Popovskiy (Ref 12) observed and investigated experimentally this dependence of the Fermi level. Thus, the position of the Fermi level also determines the catalytic activity. 1950 Vol'kenshteyn, finally also Boudart (Ref 15) and Hauffe (Ref 16). The Fermi level proved to be the

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Present State of the Electron Theory of
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key for controlling the catalytic activity on semiconductors. The "solid" acceptor binding causes a change of the potential of the surface and a compensation layer of the screening length l closely below. This changes the conductivity and thus also the yield of catalysis. Sandomirskiy (Ref 18) theoretically investigated these dependences, Gray (Ref 19), Heiland (Ref 20), Lyashenko, Stepko (Ref 21) as well as a number of foreign authors carried out also experimental investigations. They are known under the term of "marginal layer theory of adsorption". The position of the Fermi level on the surface also depends on its position in the interior of the semiconductor. This makes again possible a directing of the catalytic properties except in the case of a quasi-isolated state. On the surface a sufficient density of structural defects predominates. Catalytic activity increases in acceptor reactions, conductivity, however, decreases - vice versa in donor reactions. Adsorbability changes only with the pressure in the exterior space. Also the photoelectric effect cannot change the electrons or the electronic vacancy concentration. By the Fermi level the semiconductors prove to belong, according to their properties of adsorption and catalysis, to the crystals. There are 13 figures

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AUTHOR:

Vol'kenshteyn, E. F.

SOV/76-32-10-22/39

TITLE:

The Charging of a Semiconductor Surface During Adsorption
(O zaryazhenii poverkhnosti poluprovodnika pri adsorbtsii)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 10,
pp 2383 - 2391 (USSR)

ABSTRACT:

A representation of the adsorbed particles as "impurities" at the crystal surface was given by the author of this paper in 1948 (Ref 1). Of late a number of scientists have dealt with the problem of the charging of the surface in chemisorption; there were, for instance, Aigrain and Dugas (Egren and Dyuga) (Ref 2), Germain (Zhermen) (Ref 3), and Engel and Hauffe (Engel' and Khauffe) (Ref 4). In their papers only one type of chemisorption is investigated under the term "boundary layer theory of adsorption". In the present case the charge of the surface is investigated taking into account various types of chemisorption. It is found that the surface charge formed in the chemisorption does not only depend on the nature

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The Charging of a Semiconductor Surface During Adsorption SOV/76-32-10-22/39

of the adsorbed particles but also on the character of their binding with the surface. The chemisorbed particle can be regarded as a structural defect which has at the same time a certain affinity to the free electron as well as to the free hole (in the surface). Two types of chemisorption can be distinguished. The "weak", in which the particle adsorbed remains electrically neutral, and the "strong" chemisorption in which the particle has an electron. The latter can a) have an acceptor binding if the free electron participates in the binding of the adsorbed particle, or b) a donor binding where the free hole participates in the binding. In the considerations of the surface charge of various forms of chemisorption a paper by Sh.M.Kogan is mentioned which is in publication, as well as an equation according to the Fermi statistics. Under the same conditions the various forms of the chemisorption and therefore also the resulting electric charges of the surface depend on the chemical potential of the surface. The papers by V.B.Sandomirskiy (Refs 12-14) and V.I.

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Lyashenko and I.I.Stepko (Ref 15) as well as by S.Yu. Yelovich and L.Ya.Margolis (Ref 18) are mentioned in the connection with the effects caused by the charging of the surface. The changes between the function donor versus acceptor are explained by the various coexisting types of chemisorption on the surface. There are 5 figures and 18 references, 14 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut fizicheskoy khimii, Moskva
(AS USSR, Institute of Physical Chemistry, Moscow)

SUBMITTED: May 15, 1957

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20-118-4-34/61

AUTHORS: Ioffe, I. I., Vol'kenshteyn, F. F.

TITLE: The Trend of Contact Oxydation Reactions on
Semiconducting Catalysts (Benzene Oxydation Serving as
an Example)
(K voprosu o napravlenii reaktsii kontaktnogo okisleniya
na poluprovodnikovyykh katalizatorakh (na primere okisleniya
benzola))

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 4,
pp. 747-750 (USSR)

ABSTRACT: The authors here examine the phenomena mentioned in the
title, from the aspect of the theory of catalysis, which
was developed by F. F. Vol'kenshteyn (reference 5,6,7).
Convenient objects for the investigation of the mechanism
of the process are the simplest aromatic compounds
(benzene, naphtalene), because at them sharply marked
trends in the heterogeneous-catalytic and homogeneous
reactions are observed. The authors suppose that it is
possible to make various assumptions on the possible
mechanism of the oxydation of benzene on electron-

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The Trend of Contact Oxydation Reactions on Semiconducting Catalysts (Benzene Oxydation Serving as an Example) 20-118-4-34/61

semiconductors and Hole-semiconductors (e.g. vanadium pentoxide and cupric oxide, or cuprous oxide). Here, the authors proceed from the assumption that in case of the adsorption of benzene one of the bindings in the benzene molecule is ruptured and that the valence which has become free in this way is saturated by the free valence of the catalyst. Here are two and only two possibilities: In case of the adsorption of the benzene molecule either a C-H-binding or a C-C-binding can be ruptured. As adsorber here a crystal of the type $M_m R_r$ is examined (M denoting a metal and R a metalloid), which is regarded to be built up of the ions M^{+p} and R^{-q} ($pm = rq$). Most of the semiconductors used as catalysts (oxides, sulfides) may have a lattice of this type. First the adsorption is investigated here, in the case of which a C-H-binding is ruptured. In this case the adsorption leads to the dissociation of the benzene molecule into 2 ions, as is illustrated here schematically. This mechanism is possible in case of electron-semiconductors and also of hole-semiconductors. The

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difference between these types of semiconductors becomes noticeable in case of the interaction of the compounds, which form on the surface, with the vagrant (bluzhdet') free valences of the catalyst. Thus the electrically neutral radical which is located on the surface, forms on the hole semiconductors, whereas it practically cannot form on electron semiconductors. Then the adsorption of a benzene molecule with the rupture of a C-C-binding is investigated. Also here the process of adsorption leads to the production of a positive and of a negative valence on the surface of the catalyst, whereon the negative valence (hole) remains free and the positive valence (electron) combines with the benzene molecule, retains it on the surface, and transforms it into an electrically charged radical. Such an ion radical, which is located on the surface, practically forms only on electron semiconductors, but on hole semiconductors. The here examined hypothetical mechanism is very much schematized, it only shows the way to the understanding of the action of semiconducting catalysts in the oxydation benzene.

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The Trend of Contact Oxydation Reactions on Semiconducting Catalysts (Benzene Oxydation Serving as an Example) 20-118-4-34/61

There are 7 figures, and 15 references, 11 of which are Soviet

ASSOCIATION: Nauchno-issledovatel'skiy institut organicheskikh poluproduktov i krasiteley im. Voroshilova
(Scientific Research Institute for Organic Semiproducts and Dyes imeni Voroshilov)
Institut fizicheskoy khimii Akademii nauk SSSR
(Institute for Physical Chemistry of the AS USSR)

PRESENTED: July 8, 1957, by P. A. Rebinder, Member, Academy of Sciences USSR

SUBMITTED: April 24, 1957

AVAILABLE: Library of Congress

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20-118-5-37/59

AUTHORS: Vol'kenshteyn, F. F. , Sandomirskiy, V. B.

TITLE: The Influence of an External Electric Field on the Adsorbing Power of a Semiconductor (O vliyanii vneshnego elektricheskogo polya na adsorbtsionnuyu sposobnost' poluprovodnika)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp. 980-982 (USSR)

ABSTRACT: Here the authors designated the increase and the decrease of the adsorbing power in an electric field as electroadsorption and electrode adsorption, respectively. The present work aims at the estimation of the experimental possibility of the observation of this effect; this depends on the change of pressure in the reactor at the application of an electric field and on the field strength. The authors here investigate an adsorbent of the shape of a semiconductor plate of a thickness $2L$ in the direction of the x-axis and with sufficiently great measures in the direction of the y and z-axis. The adsorption of molecules to which the local surface levels E correspond takes place on the plane $x = \pm L$. For reasons of ex-

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The Influence of an External Electric Field on the Adsorbing Power of a Semiconductor

actness the authors investigated the adsorption of acceptor molecules on a semiconductor of the n-type. The crystal is assumed to be in an outer homogeneous electric field of the field strength F directed vertically to the surface of the crystal. The following is assumed in order to simplify the computation: a) the thickness of the crystal is much greater than the length of screening l . b) the distribution of electrons is Boltzmann-like on all energy levels in the volume of the crystal; c) surface zones are lacking; d) there exist only two kinds of bindings of the adsorbed molecules on the surface, namely, "weak" and "solid" acceptor binding. The schemes of the energy levels in the case of the lacking and of the presence of an electric field are illustrated on a diagram. The crystal is located in a reactor with the constant volume v , which is filled by a gas with the pressure p_0 . After the application of the field F gas pressure assumes the value p . The problem consists in determining the dependence of the quotient p/p_0 on F . The expression obtained for this quotient from the equation of state of the ideal gas is given here. In the case of a lacking field most of the

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adsorbed molecules are in the state of the "weak" binding on the surface. The expression for p_o/p corresponding for this case is given here. Then $p_o/p \geq 1$, i.e. in the case of the model selected here only electroadsorption is possible. The authors especially investigated the case $p_o/p \gg 1$ which corresponds to a strong effect. The dependence of the quotient p_o/o on F is given explicitly. A numerical evaluation is given at the end of this paper. There are 1 figure and 5 references, 5 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR
(Institute for Physical Chemistry AS USSR)

PRESENTED: July 25, 1957, by N. N. Semenov, Member, Academy of Sciences, USSR

SUBMITTED: July 18, 1957

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'5(4)
AUTHORS:

Vol'kenshteyn, F. F., Kogan, Sh. M.

TITLE:

Influence of the Illumination on the Adsorptive Capacity and Catalytic Activity of Semiconductors

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1536-1545 (USSR)

ABSTRACT:

The adsorptive capacity of a semiconductor is expressed by the number N of the molecules adsorbed with the gas on the surface under conditions of equilibrium. This number varies at irradiation with rays which may be absorbed by the adsorbent. The following studies in this field are quoted: Terenin (Refs 2,6), Myasnikov (Ref 5), Pshezhetskiy (Ref 5), Solonitsyn (Refs 6,7), Kiselev, Krasil'nikov, Sysoyev (Ref 8). A variation of N can be determined by changing the pressure in the adsorption space when turning irradiation on and off. In this case photo-adsorption and photo-desorption may occur, irradiation, however, can also remain inactive. The conditions for the possible three reactions are mathematically developed by means of the electron theory of semiconductors. Adsorption and desorption may occur if light causes a chemical change of the adsorbent, an apparent

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Influence of the Illumination on the Adsorptive Capacity and Catalytic
Activity of Semiconductors

chemical change, if light causes a change in the adsorbed molecule. The electron-theoretical investigation is carried out on the example of an acceptor gas and free lattice electrons. It was further assumed that adsorption is represented by solidly bound particles and desorption only by weakly bound particles. The adsorptive capacity "N" may be expressed by the probability " η " with which a particle is in a solidly bound state on the surface of the molecule. Irradiation causes a change in η . Photoadsorption occurs with an increase of η , desorption with a decrease of η (Fig 2). Value γ is introduced, which represents the change of η , in the case of $\gamma > 1$ an adsorption, in case of $\gamma < 1$ a desorption occurs; when $\gamma = 1$, however, the surface remains inactive. Finally, γ is calculated as a function of the change of the free electrons and holes of the semiconductor surface lattice. This function is dependent on frequency and intensity of the irradiated light. V. Ye. Lashkarev (Ref 13), V. P. Zhuze, and S. M. Ryvkin (Ref 14) are mentioned. There are 3 figures and 21 references, 15 of which are Soviet.

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VOLKENSHTEYN, F. F.

"General Ideas on the Electronic Theory of Catalysis of Semiconductors."

report submitted for the Second International Congress on Catalysis, Paris,
4-9 July 1960.

PHASE I BOOK EXPLOITATION

SCV/5095

Vol'kenshteyn, Fedor Fedorovich

Elektronnaya teoriya kataliza na poluprovodnikakh (Electronic Theory of Semiconductor Catalysis) Moscow, Fizmatgiz, 1960. 187 p. 10,000 copies printed. (Series: Fizika poluprovodnikov i poluprovodnikovyykh priborov)

Ed.: Ye. B. Kuznetsova; Tech. Ed.: A. P. Kolesnikova.

PURPOSE: This book is intended for physicists and chemists working in the field of catalysis, and for physicists concerned with semiconductors and the mechanism of their catalytic effect.

COVERAGE: The book is based on lectures delivered by the author at the Division of Chemistry, Moscow University, at the Jagielloński University (Poland) and at the University of Paris. It presents in concise form the present state of the electronic theory of semiconductor catalysis, emphasizing the physical rather than the mathematical fundamentals. The author thanks V. L. Bonch-Bruyevich and O. A. Golovina, who reviewed the book. ~~There~~

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VOL'KENSHTEYN F F.
PHASE I BOOK EXPLOITATION

SOV/3921

Akademiya nauk SSSR. Institut fizicheskoy khimii

Problemy kinetiki i kataliza. [t] 10: Fizika i fiziko-khimiya kataliza
(Problems of Kinetics and Catalysis. [vol.] 10: Physics and Physico-
Chemistry of Catalysis) Moscow, Izd-vo AN SSSR, 1960. 461 p. Errata
slip inserted. 2,600 copies printed.

Eds.: S.Z. Roginskiy, Corresponding Member of the Academy of Sciences USSR,
and O.V. Krylov, Candidate of Chemistry; Ed. of Publishing House: A.L.
Bankvitser; Tech. Ed.: G.A. Astaf'yeva.

PURPOSE: This collection of articles is addressed to physicists and chemists
and to the community of scientists in general interested in recent
research on the physics and physical chemistry of catalysis.

COVERAGE: The articles in this collection were read at the conference on the
Physics and Physical Chemistry of Catalysis organized by the Otdel khimicheskikh
nauk AN SSSR (Section of Chemical Sciences, Academy of Sciences USSR) and by
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Problems of Kinetics and Catalysis (Cont.)

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the Academic Council on the problem of "the scientific bases for the selection of catalysts." The Conference was held at the Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry of the AS USSR) in Moscow, March 20-23, 1958. Of the great volume of material presented at the conference, only papers not published elsewhere were included in this collection. The conference decided not to publish the discussion material. Papers by the following authors were excluded and replaced by a brief author's abstract: F.F. Vol'kenshteyn, "Surface Charge of a Semiconductor During Adsorption", M.M. Kogan and V.B. Sandomirskiy, two papers; Sh.M. Kogan, "Statistics of Adsorbed Particles in the Electron Theory of Chemisorption"; F.F. Vol'kenshteyn and Sh. M. Kogan; F.F. Vol'kenshteyn and V.B. Sandomirskiy; G.A. Korsunovskiy; A.M. Rubinshteyn, V.M. Akimov and A.A. Slinkin; L.Kh. Freydlin; V.N. Filimonov and D.S. Bystrov. The following two papers do not appear in any form in this collection because the authors did not forward the abstracts requested: M.I. Temkin, E.I. Tsybina and A.I. Gel'bshteyn, "Kinetics of Catalysis of the Vapor Phase Hydration of Acetylene by Electron Vapor Acceptors"; A.A. Babushkin, "Spectroscopic Investigation of the Structure of the Molecular Compounds of Boron Trifluoride With Nitrogen and Oxygen-Containing Molecules". Addresses to the conference by E. Kh. Yenukeyev and Ya.B. Gorokhovatskiy, are included in the form of brief communications. They cover the results of recent experimental research which could not be considered discussion material. A number of papers and communications,

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for the most part dealing with problems in the preparation of catalysts, were turned over for publication to the "Zhurnal fizicheskoy khimii". The papers of several foreign researchers who participated in the conference and those of researchers who could not participate in the conference are included in the collection: A.Bielanski, G.Deren and G. Gaber, W.K.Trzebiatowski, A.Krause (all of Poland), Wu Yüeh and Hsi Hsiao-fang (China). The editors thank Academician A.A. Balandin and G.K. Boreskov and V.V. Voyevodskiy, Corresponding Members of the AS USSR, for valuable suggestions during the compilation of the Collection. There is a bibliography of Soviet and non-Soviet sources at the end of each article.

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Problems of Kinetics and Catalysis (Cont.)

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S/195/60/001/001/001/007
B015/B06C

AUTHOR: Vol'kenshtayn, F. F.

TITLE: Basic Concepts of the Electron Theory of Catalysis on Semiconductors

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 1, pp. 32-44

TEXT: The present article is the reproduction of a lecture read at the .
Second International Congress for Catalysis and is a synopsis of the
present state of the electron theory of catalysis on semiconductors,
with special regard to the research work done by the author and his
collaborators. The main results of the theory and certain conclusions are
given, but the mathematical part of the theory is not discussed. A more
detailed survey has been supplied by the author in Vol. 12 of "Advances
in Catalysis". In the present article, the results are discussed in the
following sections: the electrically neutral and the charged forms of
chemisorption; valency-saturated and radical forms of chemisorption;
transitions among the various forms of chemisorption; equilibrium between
the various forms of chemisorption. The adsorption properties of the

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*Inst. Phys. Chem AS USSR
Moscow State Univ.*

Basic Concepts of the Electron Theory of
Catalysis on Semiconductors

S/195/60/001/001/007
B015/B060

surface; the catalytic activity of the surface; the part played by the Fermi level. Since the position of the Fermi level, which appears in all equations of the electron theory, is of special importance, several conclusions are made in this respect. Following the results of the electron theory, the conclusions drawn therefrom are discussed in the following sections: effect of chemisorption on the electrical conductivity and work function; relationship between surface and volume; correlation between catalytic activity and electrical conductivity; effect of admixtures on the catalytic activity; effect of illumination on adsorbability. The author points out that the electron theory of catalysis can by no means be regarded as final. It does not compete with the other theories of catalysis from which it differs by its problems, since it studies the elementary (microscopic) mechanism of phenomena and proceeds from this point. S. Z. Roginskiy, A. N. Terenin, V. I. Lyashenko, I. A. Myasnikov, and N. P. Keyer are mentioned in the text. There are 7 figures and 17 references: 15 Soviet, 2 US, 2 French and 1 German.

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AUTHOR:

Vol'kenshteyn, F. F., Doctor, Professor

TITLE:

The principles of the electron theory of semiconductor catalysis

PERIODICAL:

Wiadomości chemiczne, v. 14, no. 11 (161), 1960, 675-691

TEXT: The author gives a short survey of the present state of the electron theory of semiconductor catalysis. He refers to his more comprehensive study in "Advances in Catalysis", Vol. 12. The present paper was translated into Polish by: Jerzy Dereń, Doctor, Docent, and Jerzy Haber, Doctor, Docent, both Katedra Chemii Nieorganicznej Akademii Górniczo-Hutniczej w Krakowie (Department of Inorganic Chemistry of the Academy of Mining- and Metallurgy, Kraków). A paper by W. Romanowski, Doctor, appeared in this periodical, 1956, Vol. 10, p. 439 is recommended as introduction for the present paper. The author lays special emphasis upon the problems which he himself and his collaborators have studied. He lists two tasks of the afore-mentioned theory: 1. The discovery of the mechanism of electron processes to which, in the long run, every chemical reaction (also a

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catalytically heterogeneous one) is due. As long as the mechanism of individual elementary acts of catalysis is not clarified, the science of the mentioned processes will remain empirical. 2. The catalytic properties of semiconductors are closely linked with the electron processes both in the interior and on the surface of semiconductors. Since there must be an interrelation between the electron properties of a semiconductor and its catalytic properties, electron theory tries to discover the relations between these two groups of properties. The author mentions the inventor of the mentioned theory, L. W. Pisarzhevskiy (1916) and the following Soviet researchers: S. Z. Roginskiy, A. N. Terenin, W. I. Lyashenko, and I. A. Myasnikov as well as non-Soviet researchers. Modern electron theory is based (in the author's view and that of his collaborators) on the quantum-mechanical solution of the problem concerning the interaction between a foreign particle and the crystal lattice of a solid. This problem is solved by way of simple examples and, subsequently, generalized by way of more complicated cases. The author neglects the entire mathematical part and the discussion of the experimental data. The text is subdivided as follows: "The Fundamental Results of the Theory", again subdivided into: Various forms of chemisorption, chemisorption of

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particles with saturated valencies as well as of radicals, passing over from one form of chemisorption to another, equilibrium between these forms, adsorptive power of the surface, the capability of the surface of catalysis, the role of the Fermi level. The next chapter: "Some Important conclusions" contains the following sections: Effect of chemisorption upon the electrical conductivity and upon the work function, interaction between the surface and the interior of a crystal. Relation between the catalytic activity and the electrical conductivity, effect of admixtures upon the catalytic activity, effect of light upon the adsorptive power. Finally the author describes the present state of this theory as follows: The electron theory proves that both free electrons and semiconductor holes take part in the formation of chemisorptive bonds: the electrons and holes play the part of free valencies, in which case the strength of bonds and the reactivity of the chemisorbed particles depends on the degree of participation of electrons and holes. Therefore, the Fermi level occurs in all formulas of the electron theory. The catalytic and absorption properties of the semiconductor surface are, by the Fermi level, closely linked with the state of the crystal as a whole. As this paper shows, the electron theory may be interpreted in three ways: a. By illustrative models; b. By

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using the valencies lines, e.g., when describing the chemical part of the phenomena (Figs. 2 and 3); c. On the basis of the energy zone scheme with the aid of which the electron mechanism of the phenomena is studied (example: Figs. 4a and 7). The author emphasizes that each problem may be illustrated by one of the mentioned models. In his opinion, the theory cannot be regarded as complete. He states furthermore that this theory does not compete with any theory of catalysis. It differs by the manner in which the problem is posed. The electron theory seeks to approach the problem by detecting the elementary mechanism of the phenomenon. The relation between the existing phenomenological theories on the one hand, and the electron theory on the other, is the same as, e.g., that of the theory of the chemical bond of the nineteenth century, which exclusively used valency lines and the modern quantum-mechanical theory of the bond. It was the modern theory which gave the valency lines their physical sense, thus discovering the physical nature of the chemical forces. There are 7 figures and 19 references: 17 Soviet-bloc and 2 non-Soviet-bloc.

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The principles of the electron...

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry of the Academy of Sciences USSR). Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Moscow State University imeni M. V. Lomonosov)

SUBMITTED: June 6, 1960

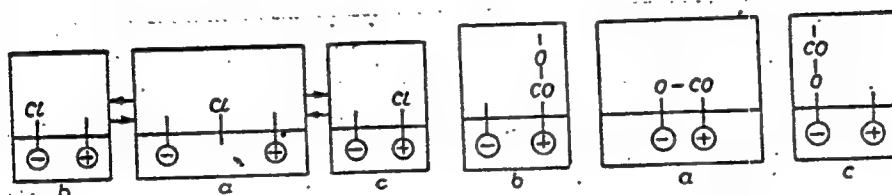


Fig. 2

Fig. 3

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Legend to Fig. 4a: A - donor level
D - acceptor level.

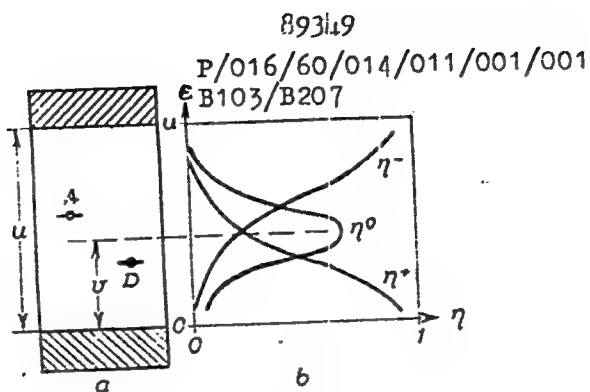
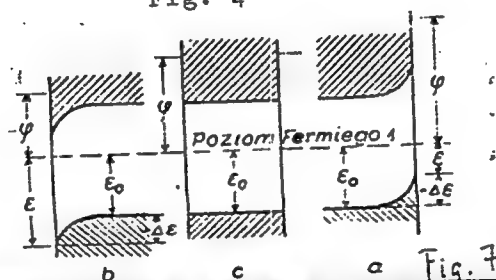


Fig. 4

Legend to Fig. 7: 1) Fermi level.



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B015/B056

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AUTHORS:

Vol'kenshteyn, F. F. and Kogan, Sh. M.

TITLE:

The Concept of the "Quasi-insulated" Surface in the Theory of Chemisorption ¹

PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 9,
pp. 1996-2004

TEXT: This is a discussion on semiconductors ²⁴ in which the surface states have a denser structure than the interior of the body, which is the case if the semiconductor has a real and not an idealized surface. Besides, the concentration of the electrons and holes which are localized on the surface, may be very high. It is shown in this case the position of the Fermi level F_S on the crystal surface is independent of the position of the Fermi level F_V in the interior of the crystal, which means that also the chemisorption- and catalytical properties of the semiconductor surface are independent of the electronic properties in the interior of the crystal. Surfaces of this kind are described by the authors as

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in the Theory of Chemisorption

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"quasi-insulated", and occur whenever the absolute value of the difference between the positive and negative charges localized on the surface is small in comparison to their sum. In the case of "quasi-insulated" surfaces, the influence of the crystal impurities upon the chemisorption and catalytic properties vanishes, and only the structure of the surface is significant. Several specific properties of the "quasi-insulated" surface are explained, and three types of surface states are mentioned, which lead to a "quasi-insulated" surface. There are 1 figure and 10 references: 9 Soviet and 1 US.

ASSOCIATION: Akademiya nauk SSSR Institut fizicheskoy khimii (Institute
of Physical Chemistry of the Academy of Sciences USSR).
Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: December 22, 1958

Card 2/2

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E036/E455

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AUTHOR: Vol'kenshteyn, F.F.

TITLE: Influence of ionizing radiation on the adsorption and catalytic properties of semiconductors

PERIODICAL: Kinetika i kataliz, v.2, no.4, 1961, 481-489

TEXT: In this article the effect of ionizing radiation on the adsorption and catalytic properties of semiconductors is examined in the light of the electron theory of chemisorption and catalysis. The mechanism by which the radiation influences the adsorption equilibrium, the kinetics of adsorption and the rate of catalytic reaction is analysed and is derived directly from the general concept of electron theory. The dependence of the radiation effect on temperature and pressure and on the history of the sample is considered. The effect of radiation on catalytic processes and adsorption has been well established by experimental work over the last few years but the mechanism remains unknown. The present article is limited to establishing some general laws derived from electron theory. The following three effects are obtained during irradiation: (a) direct ionization; (b) change of

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degree of disorder in the lattice and (c) nuclear reactions. All these give rise to a change in the concentration of free carriers. In the first of the three cases, this change is due to non-equilibrium carriers and, in the other two cases, to displacement of the electron equilibrium. The first effect disappears when irradiation ceases; the second may be considered as due to sample heating. The third effect is irreversible and arises from the introduction of chemically foreign impurities. According to the electron theory of catalysis and adsorption, the free carriers participate directly in chemical processes at the surface. The carriers behave as free valence electrons and thus the concentration change gives rise to a change in adsorption and catalytic properties. Electrically, the surface particle may be neutral or negatively or positively charged, exhibiting correspondingly different bond characteristics, bond strengths and reaction ability. The various reaction abilities depend upon whether the state is valence-satisfied or involves radicals or ionic radicals. The expressions for the relative concentrations of these states in the unirradiated condition are written down for equilibrium. The negative- and the positively-charged particles

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are considered as localized acceptor and donor levels respectively. The expressions have been given by the author in Ref.1 (The electron theory of catalysis in semiconductors, Fizmatgiz, M., 1960) in terms of the difference between the levels and the conduction or valence bands and the Fermi level at the surface. Some simple expressions are then written down in terms of the carrier concentrations in the presence and absence of irradiation. In these expressions, the relative numbers of particles in the three states of the radiated sample are related to those in the unirradiated sample. If the condition before equilibrium is considered, quasi-Fermi levels must be introduced. These derivations have either been obtained by the author in previous work (Ref.1: as quoted in text and Ref.3: Izv. AN SSSR Otd. khim. n., 1959, 1536) or may be derived by analogy. It is shown that irradiation gives effects equivalent to displacement of the localized acceptor and donor levels in the energy scheme. The amount of the displacement depends on the position of the level in the energy scheme and on the conditions of irradiation. The change in the adsorbing properties of the surface during irradiation is indicated by a change in the pressure ΔP in the

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volume of the phase being adsorbed when the radiation is applied. ΔP is related simply to the change in the total number of particles in the equilibrium conditions of the sample with and without irradiation. It is shown that the sign and relative magnitude of ΔP depend on the position of the Fermi level in the original, unirradiated sample. The point at which the change of sign occurs - the change from desorption to adsorption or the reverse - is dependent on the conditions of irradiation. This simple treatment can be used to interpret the results given by Y. Fujita, T. Kwan (Ref. 4: Bull. Chem. Soc. Japan, 31, 379, 1958) and by A. N. Terepin, Yu. P. Solonitsyn (Ref. 5: Disc. Faraday Soc., v. 28, 28, 1959). In general, the change of adsorbing properties due to irradiation depends on the nature of the radiation, on the pressure of the gaseous phase, on temperature and on the previous history of the sample. All these factors are evident from the analysis. For simplicity, only a small degree of filling of the levels is assumed, an assumption made in the analysis of the kinetics of adsorption. Here expressions are derived for the pressure in the volume of particles being adsorbed: the pressure is given as a function of time and in terms of the number of

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particles adsorbed. The relative number of neutral particles is the ratio of neutral particles to the total number of particles. The ratio is assumed to be independent of the pressure which implies that the change in surface charge due to adsorption may be neglected and is due only to non-adsorption processes. A similar exponential expression is quoted for the irradiated case. The subsequent analysis is restricted to the case of acceptor particles. It is shown that the sensitivity of the kinetics - the variation of pressure with time - can be varied by the impurity content of the sample, which determines the position of the Fermi level. In addition to this simple case, where adsorption commences at a time $t = 0$, the article considers adsorption on a sample which first remains unirradiated up to time t_1 , after which the radiation is applied until $t = t_2$ and then ceases. In Fig.4 the curves of pressure of the phase being adsorbed are plotted as functions of time in some typical experiments of this type. Similar curves are observed experimentally. The dotted lines correspond to behaviour in the absence of irradiation. Note that the subscript "o" denotes absence of irradiation. The light lines denote continuous irradiation from $t = 0$ to $t = \infty$.
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The various cases correspond to differing initial conditions of the sample, the position of the Fermi level and to the differing nature of the irradiation. It is seen that both desorption (Fig.4a) and slowing down of adsorption (Fig.4b) are possible on commencing irradiation and that the effects may be reversible (Fig.4c) or irreversible (Fig.4d). The time at which the radiation is applied is also important. For catalytic effects the case of the oxidation of CO is considered. Again the analysis of Ref.1 is quoted for donor- and acceptor-type actions, giving expressions for reaction rates in terms of the Fermi level position and the levels corresponding to the molecule CO₂ and the atom O. The irradiation conditions and the position of the Fermi level in the irradiated specimen can enhance or reduce the reaction rate, but the ratio of the partial pressures of O₂ and CO enter as a further variable. Again the experimental results can be discussed qualitatively in terms of this model. Impurities in the semiconductor affect catalysis: this action can also be described by the same model. All the phenomena discussed depend on a parameter which is a function of the acceptor energy level, the initial Fermi level and the quasi-

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Fermi levels for holes and electrons arising during irradiation. A similar parameter is required for donor-like particles. At no stage in the paper is a quantitative evaluation attempted. Among the effects ignored is the possibility of impurities diffusing from the semiconductor bulk towards the surface and reacting with the adsorbed ions. There are 5 figures and 10 references: 5 Soviet-bloc and 5 non-Soviet-bloc. The four most recent references to English language publications read as follows:

Ref.4: as quoted in the text;

Ref.6: T.I.Barry, Report on the Second International Congress on Catalysis, Paris, 1960;

Ref.7: F.Romero-Rossi, F.S.Stone, Report on the Second International Congress on Catalysis, Paris, 1960;

Ref.10: T.I.Barry, F.S.Stone, Proc. Roy. Soc., A255, 124, 1960.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR
(Institute of Physical Chemistry AS USSR)

SUBMITTED: March 3, 1961

Card 7/87

VOL'KENSHTEYN, F.F., doktor fiziko-matematicheskikh nauk, prof.

Semiconductors as catalysts. Nauka i zhizn' 28 no.8:11-15

Ag '61.

(MIRA 14:8)

(Semiconductors) (Catalysts)

BALANDIN, A.A., akademik, red.; KOBOZEV, N.I., prof., red.; LEBEDEV, V.P., dots., zam. red.; MAL'TSEV, A.N., zam. red.; AGROMOV, A.Ye., dots., zam. red.; TOPCHYEVA, K.V., prof., red.; YUR'YEV, Yu.K., prof., red. PANCHENKOV, G.M., prof., red.; SOKOL'SKIY, D.V., akademik, red.; VOL'KENSHTLYN, F.F., prof., red.; LAZAREVA, L.V., tekhn. red.

[Catalysis in the institutions of higher learning; papers of the First Interuniversity Conference on Catalysis] Kataliz v vysshei shkole; trudy. Moskva, Izd-vo Mosk. univ. No.1. Pt.2. 1962. 325 p. (MIRA 15:10)

1. Mezhvuzovskoye soveshchaniye po katalizu. 1st, 1958. 2. Akademiya nauk Kazakhskoy SSR (for Sokol'skiy). ~~3. Khimicheskiy fakul'tet~~ Moskovskogo gosudarstvennogo universiteta (for Yur'yev). (Catalysis)

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EWI(1)/EWG(k)/BDS

AFFTC/ASD/ESD-3/IJP(C)

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ACCESSION NR: AT3002446

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65
63

AUTHOR: Vol'kenshteyn, F. F.; Karpenko, I. V.

TITLE: Theory of photoadsorption effect on semiconductors ²¹ [Report at the Conference on Surface Properties of Semiconductors, Institute of Electrochemistry, AN SSSR, Moscow, 5-6 June 1961]

SOURCE: Poverkhnostnyye svoystva poluprovodnikov. Moscow, Izd-vo AN SSSR, 1962, 114-127.

TOPIC TAGS: semiconductor, semiconductor theory, photoadsorption effect

ABSTRACT: A further development is offered of the theory of photoadsorption effect (variation of adsorbability with illumination). Specifically, a criterion is established which determines the sign (plus-minus) of photoadsorption effect under various conditions: adsorbent and adsorbate nature, pressure, temperature, specimen prehistory, etc. The sign depends on the position of the Fermi level and on the degree of band bending. The theory is checked against the published experimental data obtained by F. Romero-Rossi, F. S. Stone, T. I. Barry, Y. Fujita, T. Kwan, A. N. Terenin, Y. P. Solonitzin, and others. Orig. art. has: 2 figures and 22 formulas.

ASSN: INSTITUTE OF PHYSICAL CHEMISTRY, AN SSSR; MOSCOW STATE UNIVERSITY.

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L 18992-63 EPF(c)/EWT(1)/EWP(q)/EWT(m)/BDS AFFTC/ASD/ESD-3/
IJP(C) Pr-4 GG/RM/WW/JD/MAY/JFW/JG

ACCESSION NR: AT3002452

S/2935/62/000/000/0179/0192 74
73

AUTHOR: Vol'kenshteyn, F. F.; Gorban', A. N.; Sokolov, V. A,

TITLE: Processes of recombination of free radicals on a semiconductor surface
and their role in luminescence [Conference on Surface Properties of Semiconductors,
Institute of Electrochemistry, AN SSSR, Moscow, 5-6 June, 1961]

SOURCE: Poverkhnostnyye svoystva poluprovodnikov. Moscow, Izd-vo AN SSSR,
1962, 179-192

TOPIC TAGS: semiconductor, semiconductor-surface characteristics,
luminescence, surface recombination

ABSTRACT: On the basis of the electronic theory of chemosorption and catalysis,
the radical-recombination mechanism of luminescence is examined, as well as
some consequences ensuing from that mechanism. A theoretical and experimen-
tal investigation is reported of the effect of an external transverse electric field
upon the intensity of candoluminescence. Luminescence is considered as
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ACCESSION NR: AT3002452

consisting of two steps: ionization and neutralization of an activator atom; the accompanying phenomena are explained and pictorially represented. A new formula describing the intensity of luminescence is developed, and the effect of the Fermi level on the intensity is investigated. The effect of the electric field on candoluminescence was studied in a special device on a ZnS-CdS copper-activated phosphor placed in a low-temperature lighting-gas ⁵ flame. Potentials -2kv and +2kv were applied to the electrodes producing the electric field in the phosphor zone, and the variation in the luminescence intensity was measured. The experiments are interpreted as corroborating the probability of the radical-recombination mechanism. Orig. art. has: 7 figures and 26 formulas.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AN SSSR); Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry, AN SSSR)

SUBMITTED: 00

DATE ACQ: 15May63

ENCL: 00

SUB CODE: PH

NO REF SOV: 009

OTHER: 002

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ENP(q)/EWT(m)/BDS AFFIC/ASD JD/AB

ACCESSION NR: AT3002453

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62
59

AUTHOR: Vol'kenshteyn F. F.; Kuznetsov, V. S.; Sandomirskiy, V. B.

TITLE: Chemosorptional and catalytic properties of semiconductor film on metal [Conference on Surface Properties of Semiconductors, Institute of Electrochemistry, AN SSSR, Moscow, 5-6 June, 1961]

SOURCE: Poverkhnostnyye svoystva poluprovodnikov. Moscow, Izd-vo AN SSSR, 1962, 192-206

TOPIC TAGS: chemosorption, semiconductor, catalysis, semiconductor-coated metal

ABSTRACT: Since many metals are always coated with a binary-compound film, chemosorption and catalytic processes actually transpire on the surface of a semiconductor. A theoretical investigation is offered of these processes. A rather thick semiconductor film that does not contain surface states and a positive contact potential difference are assumed; four energy schemes are

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3
considered. Qualitative properties of the film adsorbability and its catalytic activity are described by a set of differential equations. The effect of the film thickness on the work function is explored. It is found that: (1) With a specified nature and thickness of the film, its adsorbability with respect to a donor (acceptor) gas will be higher (lower) with a higher work function of the underlying metal, irrespective of the sign of the surface charge on the film; and (2) A similar relation exists between the catalytic film activity and the donor (acceptor) reaction. Orig. art. has: 3 figures and 36 formulas.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry, AN SSSR); Institut radioelektroniki AN SSSR (Institute of Radio and Electronics, AN SSSR); Institut kataliza AN SSSR (Institute of Catalysis, AN SSSR)

SUBMITTED: 00

DATE ACQ: 15May63

ENCL: 00

SUB CODE: PH

NO REF SOV: 002

OTHER: 001

Card 2/2

24.7400 (1055, 1160, 1454)

35063
S/195/62/003/001/004/010
E039/E136

AUTHORS: Vol'kenshteyn, F.F., and Karpenko, I.V.

TITLE: On the theory of the photoadsorption effect in
semiconductors

PERIODICAL: Kinetika i kataliz, v.3, no.1, 1962, 72-80

TEXT: The exposure of semiconductors to light sometimes stimulates a change in the adsorptive capacity of the surface; in some cases there is an increase in adsorption and in others a decrease. The existing experimental data appear to be inconsistent, but in this paper a theory is advanced, based on the electronic theory of chemisorption, which explains these positive and negative adsorption effects. The concentrations corresponding to free electrons and holes in the surface of a semiconductor are represented by n_0 and p_0 in the absence of light and the corresponding changes in concentration stimulated by exposure to light are Δn_s and Δp_s . The authors use the expression:

X

Card 1/7

On the theory of the photoadsorption... S/195/62/003/001/004/010
E039/E136 .

$$\gamma = \frac{\Delta n_s}{n_{os}} \cdot \frac{p_{os}}{\Delta p_s} \cdot \exp \left[\frac{(\epsilon - V_{os} + v)/kT}{1} \right] - 1 \quad (1)$$

where the meanings of the values ϵ , V_{os} and v are evident from Fig.1, which represents an energy diagram for a semiconductor with a negatively charged surface. The line FF is the Fermi level in the non-illuminated condition. A is the local surface level (acceptor and donor) representing adsorption of particles. The sign of the photoadsorption effect depends on the sign of γ , and the problem reduces to a calculation of the quantities Δn_s and Δp_s . The final expressions obtained are:

$$\begin{aligned} \Delta n_s &= (I_o + j_s) \sqrt{\frac{\tau_i}{D_i}} \exp(-V_{os}/kT) \\ \Delta p_s &= (I_o + j_s) \sqrt{\frac{\tau_i}{D_i}} \exp(+V_{os}/kT) \end{aligned} \quad (18)$$

Card 2/5

On the theory of the photoadsorption... S/195/62/003/001/004/010
E039/E136

where I_0 is the intensity of the light. It is shown that the sign of γ is determined by the sign of ψ where

$$\psi = \epsilon + V_{os} - v \quad (19)$$

Hence we have:

(a) For acceptor particles:

Positive effect (photoadsorption) if $\psi < 0$,

Negative effect (photodesorption) if $\psi > 0$.

(b) For donor particles:

Positive effect (photoadsorption) if $\psi > 0$,

Negative effect (photodesorption) if $\psi < 0$.

The results are discussed in detail and the theory compared with experimental data; in particular for the case of adsorption of oxygen on zinc oxide. The sign of the effect depends on the pressure, temperature and also the presence of excess zinc in the ZnO samples. There are 3 figures. ✓

Card 3/5

On the theory of the photoadsorption... S/195/62/003/001/004/010
E039/E136

ASSOCIATION: Institut fizicheskoy khimii AN SSSR
(Institute of Physical Chemistry, AS USSR)
Moskovskiy gosudarstvennyy universitet im.
M.V. Lomonosova
(Moscow State University imeni M.V. Lomonosov)

SUBMITTED: September 28, 1961

Card 4/5

5.4/00

h2169

S/195/62/003/005/003/007

E039/E135

AUTHORS: Vol'kenshteyn, F.F., Kuznetsov, V.S., and
Sandomirskiy, V.B.

TITLE: The chemisorption and catalytic properties of
semiconducting films on metals.

PERIODICAL: Kinetika i kataliz, v.3, no.5, 1962, 712-723

TEXT: The case of a metal covered with a plane parallel film
of uniform semiconductor (e.g. its oxide) containing donor and
acceptor centres uniformly distributed throughout its volume is
treated theoretically. Energy diagrams are given for coatings
with a thickness L greater than the screening length ℓ and for
the case when $L \leq \ell$ with a net positive or negative surface
charge. Owing to mathematical difficulties only the sign of the
following derivatives is determined for the various conditions:

$$\left. \begin{array}{l} (d\epsilon/dL)_{p, T, \chi} \\ (d\epsilon/d\chi)_{p, T, L} \end{array} \right\} ; \quad (7)$$

Card 1/3

The chemisorption and catalytic ...

S/195/62/003/005/003/007
E039/E135

$$\left. \begin{aligned} (d\theta/dL)_{p, T, \chi} &= (d\theta/d\varepsilon)_{p, T} \cdot (d\varepsilon/dL)_{p, T, \chi} \\ (d\theta/d\chi)_{p, T, L} &= (d\theta/d\varepsilon)_{p, T} \cdot (d\varepsilon/d\chi)_{p, T, L} \end{aligned} \right\} ; \quad (8)$$

$$\left. \begin{aligned} (dg/dL)_{p, T, \chi} &= (dg/d\varepsilon)_{p, T} \cdot (d\varepsilon/dL)_{p, T, \chi} \\ (dg/d\chi)_{p, T, L} &= (dg/d\varepsilon)_{p, T} \cdot (d\varepsilon/d\chi)_{p, T, L} \end{aligned} \right\} . \quad (9) \quad \checkmark$$

Here: ε is the work function of the film, characterised by the position of the Fermi level at the external surface of the film; χ is the work function of the metal; θ is the adsorptive capacity of the film; g is the rate of reaction. It is shown that the adsorptive capacity and catalytic activity and selectivity depend on the thickness of the film. Experimental verification of this work is required. It should be noted that for L to be less than λ requires coating thicknesses of less than 10^{-4} - 10^{-5} cm and for the coating to be considered as an independent phase L must be greater than 10^{-6} cm. There are 3 figures.
Card 2/3

The chemisorption and catalytic ...

S/195/62/003/005/003/007
E039/E135

ASSOCIATION: Institut fizicheskoy khimii AN SSSR
(Institute of Physical Chemistry, AS USSR)

Institut kataliza SO AN SSSR
(Institute of Catalysis, SO AS USSR)

Institut radiotekhniki i elektroniki AN SSSR
(Institute of Radioengineering and Electronics,
AS USSR)

SUBMITTED: February 16, 1962

Card 3/3

S/195/63/004/001/001/009
E075/E436

AUTHORS: Vol'kenshteyn, F.F., Gorban', A.N., Sokolov, V.A.

TITLE: The processes of recombination of free radicals on the surfaces of semiconductors and their role in luminescence

PERIODICAL: Kinetika i kataliz, v.4, no.1, 1963, 24-34

TEXT: The authors examined the theory of luminescence based on the recombination of radicals at the semiconductor surfaces and investigated the influence of external transverse electrical field on the intensity of candoluminescence. The luminescence was stated to be caused by the combination of ionized atoms with electrons from the solid lattice, the formation of ions being due to chemisorption. Electron exchange resulted between the local levels of chemisorbed atoms and the lattice energy zones. The exchange with the valency zones was thermal in character, whilst the exchange with the conductivity zones resulted from the recombination of radicals. The luminescence was produced only when the recombination occurred between chemisorbed atoms and atoms from the gaseous phase. The intensity of luminescence was determined by the Fermi level on crystal surfaces and given by Card 1/3

S/195/63/004/001/001/009
E075/E436

The processes of recombination ...

$$I = A \left[1 + B \exp \left(\frac{\epsilon - v}{kT} \right) \right]^{-1} \quad (23)$$

$$\begin{cases} A = \alpha N^M P \\ B = 1 + \frac{b}{P} \end{cases} \quad (24)$$

where N^M - maximum number of atoms that can be adsorbed per unit surface, P - partial gas pressure, b - adsorption coefficient depending on temperature T , ϵ - energy level above the Fermi level, to which a surface electron is raised after a recombination act, v - total energy of the lattice electron. At $P = \infty$, $\epsilon_M = v$. The condition favorable for the radical-recombination luminescence is $\epsilon < \epsilon_M$ (26) where

$$\epsilon_M = v - kT \log \left(1 + \frac{b}{P} \right), \quad I_M = \frac{1}{2} \alpha N^M P \quad (25)$$

When the Fermi level is depressed, the intensity of luminescence increases and vice versa. This confirms the conditions given
Card 2/3

The processes of recombination ...

S/195/63/004/001/001/009
E075/E436

by Eq.(26). The experimental results agree qualitatively with the developed theory. There are 7 figures.

ASSOCIATION: Tomskiy politekhnicheskiy institut
Institut fizicheskoy khimii AN SSSR
(Tomsk Polytechnic Institute
Institute of Physical Chemistry AS USSR)

SUBMITTED: September 18, 1961

Card 3/3

L 1115-66 EWT(1)/EWT(m)/EPF(c)/EWP(j)/I/EWA(h) IJP(c)/RPL AT/RM/GS

ACCESSION NR: AT5020492

UR/0000/64/000/000/0457/0462

AUTHORS: Vol'kenshteyn, F. F.; Gorban', A. N.; Sokolov, V. A. 81
3+1

TITLE: On the problem of semiconductor luminescence resulting from the recombination of free atoms and radicals on the surface

SOURCE: Mezhevuzovskaya nauchno-tekhnicheskaya konferentsiya po fizike poluprovodnikov (poverkhnostnyye i kontaktnyye yavleniya). Tomsk, 1962. Poverkhnostnyye i kontaktnyye yavleniya v poluprovodnikakh (Surface and contact phenomena in semiconductors). Tomsk, Izd-vo Tomskogo univ., 1964, 457-462

TOPIC TAGS: semiconducting material, luminescence, free radical, electric field, zinc sulfide, cadmium sulfide, Fermi level

ABSTRACT: A mechanism of radical-recombination luminescence is proposed, and an experiment conducted to confirm aspects of the theory of semiconductor luminescence is described. The work was performed to supplement the authors' earlier research in this area. Tests were run to determine the effect of a field on luminescence. Radicals of hydrogen and air were formed by electric discharge (+5 kV) under a pressure of ~1mm Hg in a tube about 2 m long and 3 cm in diameter, containing ZnS and CdS-Cu phosphor. The experimental results confirmed qualitatively

Card 1/2

L 1115-66

ACCESSION NR: AT5020492

that the intensity of luminescence is dependent upon the location of the Fermi level and confirmed also the theoretically expected effect of an electric field on the adsorptivity of a semiconductor surface. Orig. art. has: 2 diagrams, 2 graphs, 1 table, and 9 formulas.

ASSOCIATION: none

SUBMITTED: 06Oct64

ENCL: 00

SUB CODE: SS

NO REF SOV: 007

OTHER: 002

Card ^{KC} 2/2

L 19639-65 EWG(j)/EWT(1)/EWG(k)/EWT(m)/EPF(c)/EWP(j)/T/HWA(h)/EWA(1)
Pz-6/Pc-4/Pr-4/Peb BSD/ASD(a)-5/AFWL/SSD/DIAAP/IJP(c) AT/RM

ACCESSION NR: AP5000481

S/0062/64/000/011/1935/1943

AUTHOR: Baru, V. G.; Vol'kenshteyn, F. F.

TITLE: Probable explanation of the effect of radioactive additives on the chemisorption and catalytic properties of semiconductors

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 11, 1964, 1935-1943

TOPIC TAGS: semiconductor crystal, nonmetallic crystal, radiation effect, crystal self irradiation, radioactive additive effect, chemisorption theory, catalysis theory

ABSTRACT: A theoretical study of the changes in adsorptive capacity and catalytic activity of nonmetallic semiconductor crystals self-irradiated by radioactive additives has been presented from the standpoint of the electronic theory of chemisorption and catalysis. The relative changes in the properties were correlated with the changes in the concentration of free electrons or holes on the surface of a radioactive sample. Calculation of the concentration changes was made on the assumption of simultaneously radiation-induced electronic ex-

Card 1/3

L 19639-65

ACCESSION NR: AP5000481

citation and ionization processes. Possible radiation-induced crystal-lattice defects and chemical transformations were neglected. Mathematical expressions of the excitation and ionization effects were derived as functions of the specific radioactivity of the sample. It was shown that the mechanism of the overall radiation effect is determined by the value of specific radioactivity, R . At small values of R , the main factor is excitation; at large values of R , the ionization process prevails. Both mechanisms contribute equally to the overall radiation effect at a value R_0 of specific radioactivity, which depends on the history of the sample. This particular value, R_0 , might be shifted one way or another by an appropriate treatment of the samples. The shift in R_0 value might cause a change in the magnitude and sign of the overall radiation effect, which consequently depends on the history of the adsorbent (catalyst) and on experimental conditions. The change in the sign of R_0 was observed experimentally by A. A. Balandin, V. I. Spitsyn, et al. [Izv. AN SSSR. Otd. khim. n. 1961, 4] in the catalytic dehydration of isopropylalcohol. Orig. art. has: 2 figures and 49 formulas.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry, Academy of Sciences, SSSR)

Card: 2/3

L 39236-65 EWT(1)/EWT(n)/T/EWA(h) Pz-6/Pob IJP(c) AF
 S/0195/65/006/001/0095/0107 33
 31
 B
 21

ACCESSION NR: AP5006776

AUTHOR: Volkenshteyn, F. F., Peshev, O.

TITLE: The electron factor in the kinetics of chemisorption on semiconductors

SOURCE: Kinetika i kataliz, v. 6, no. 1, 1965, 95-107

TOPIC TAGS: chemisorption, kinetics, semiconductor

ABSTRACT: The kinetics of chemisorption on semiconductors is investigated within the framework of the electron theory. It is assumed that the particles which are held by chemical forces are of the acceptor type. In other words these particles may be electrically neutral (weak surface interaction) or negatively charged (strong surface interaction) and may pass from one state to the other. Let $N^0 = N^0(t)$ and $N^- = N^-(t)$ be the surface concentrations of the neutral and the negatively charged particles respectively, while $N(t) = N^0(t) + N^-(t)$ is the total number of chemisorbed particles of a given type on a unit of the surface at a given time t . If a state of electron equilibrium exists on the surface at the time t , the relative content of the charged and neutral forms of chemisorption on the surface at this moment is given by the Fermi-Dirac statistical formulas:

Card 1/4

1-39736-65

ACCESSION NR: AP5006776

$$\begin{aligned} \eta^-(t) &= \frac{N^-(t)}{N(t)} = \left[1 + \exp \frac{e_s^-(t) - \sigma^-}{kT} \right]^{-1} = \left[1 + \exp \frac{e_s^-(t) - e_s^+(t)}{kT} \right]^{-1} \\ \eta^+(t) &= \frac{N^+(t)}{N(t)} = \left[1 + \exp \frac{\sigma^- - e_s^-(t)}{kT} \right]^{-1} = \left[1 + \exp \frac{e_s^+(t) - \sigma^+}{kT} \right]^{-1} \end{aligned} \quad (1)$$

The notation used here will be clear from an examination of Fig. 1 of the Enclosure which gives the band diagram of a semiconductor with a negatively charged surface. A is the localized level of the chemisorbed particle; FF is the Fermi level. The average lifetime of a particle in the chemisorbed state is designated by τ , while τ^0 and τ^- designate the average lifetimes of neutral and charged chemisorbed particles. The authors show that condition (1) may be considered approximately fulfilled only when t is much greater than τ^- , i.e. a state of electron equilibrium is reached on the surface during adsorption if $\tau^0, \tau \ll \tau^-$ while in the opposite limiting case $\tau \ll \tau^0, \tau^-$ electron and adsorption equilibrium states are reached simultaneously. In the latter case, the energy of adsorption activation depends on the electron state of the system. One or the other of these two limiting cases may occur depending on the nature of the adsorbent and the adsorbate.

Card 2/4

L 39736-65

ACCESSION NR: AP5006776

Desorption kinetics is also studied (pressure maintained at zero). In the first limiting case, electron equilibrium is maintained during desorption (desorption is complete in this case). However in the second limiting case electron equilibrium breaks down during desorption. Desorption in this case is only partially completed (the case of partially irreversible adsorption). The relative content of reversible and irreversible forms of chemisorption on the surface depends on the nature of the adsorbent. Adsorption and desorption kinetics are examined in detail for these two cases. Orig. art. has: 3 figures, 40 equations.

ASSOCIATION: Institut fizicheskoy khimii AN SSSR (Institute of Physical Chemistry, Academy of Sciences SSSR); Fizicheskiy fakul'tet Moskovskogo gosudarstvennogo universiteta im. M. V. Lomonosova (Department of Physics, Moscow State University)

SUBMITTED: 20Feb64

ENCL: 01

SUB CODE: GC, EC

NO REF SOV: 003

OTHER: 010

Card 3/4

VOL'KENSHTEYN, I.I.

Electronic factor in catalysis and the problem of selecting
catalysts. Zhur. fiz. khim. 39 no.8:1809-1816 Ag '65.
(MIRA 18:9)

1. Institut fizicheskoy khimii AN SSSR.

L 18570-66 EWT(m)/T

ACC NR: AP6002430

SOURCE CODE: UR/0020/65/165/005/1101/1104

AUTHORS: Vol'kenshteyn, F. F.; Karpenko, I. V.

ORG: Institute of Physical Chemistry, Academy of Science SSSR (Institut fizicheskoy khimii Akademii nauk SSSR)

41
B

TITLE: Displacement of the adsorption equilibrium on the surface of a semiconductor due to illumination

44.55

SOURCE: AN SSSR. Doklady, v. 165, no. 5, 1965, 1101-1104

TOPIC TAGS: semiconductor theory, semiconductor research, semiconductor conductivity, photoeffect, gas adsorption, semiconductor

ABSTRACT: The authors attempt a theoretical treatment of the photoadsorption effect and present a discussion which is an extension of their previous work on the same topic (Kinetika i kataliz, 3, 72, 1962). The discussion is based on the following, explained by a model shown in Fig. 1, where A is the localized surface level of the chemisorbed particle, FF - Fermi level in the nonilluminated specimen, and all other quantities are defined as in F. F. Vol'kenshteyn (Kinetika i kataliz, 2, 481, 1961). On the basis of the proposed model, it is concluded

Card 1/3

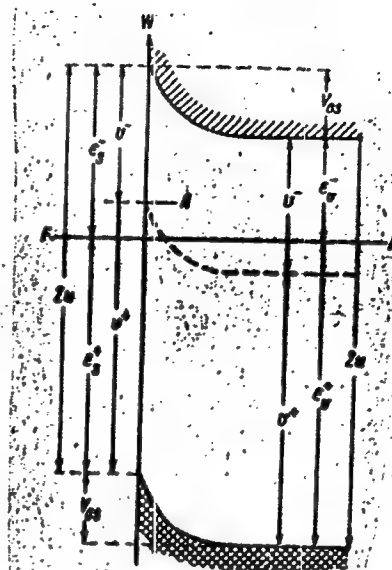
UDC: 541.183.03

2

L 18570-66

ACG NR: AP6002430

Fig. 1. Schematic of the energy level distribution for the proposed model of the photoadsorption effect.



that there should exist a correlation between the photoadsorptive effect and the

Card 2/3

Card 2/3

L 18570-66

ACC NR: AP6002430

work function of the semiconductor surface. The equation for the inversion point of the photoadsorptive effect is derived as

$$\Phi = \Phi_M = \psi/b = I \exp(\psi \mp V_{os})$$

where ϕ is defined by

$$\phi = \frac{N - N_0}{N_0} = \frac{\Delta N}{N_0}$$

in which N and N_0 are the surface concentrations of the chemisorbed particles in the presence and absence of illumination respectively. V_{os} is the work function, I is the light intensity, and ψ is defined in Fig. 1. It is stated that more experimental work is necessary before a conclusive test of the proposed theory for the photoadsorption effect can be made. This paper was presented by Academician M. M. Dubinin on 28 July 1965. Orig. art. has: 2 graphs and 11 equations.

SUB CODE: 20/ SUBM DATE: 26Jul65/ ORIG REF: 005/ OTH REF: 001

Card 3/3 *SMC*

FIGUROVSKAYA, Ye.N.; KISELEV, V.F.; VOL'KENSHTEYN, F.F.

Effect of chemisorption of oxygen on the work function and
conductance of titanium dioxide. Dokl. AN SSSR 161 no.5:1142-
1145 Ap '65.

(MIRA 18:5)

1. Moskovskiy gosudarstvennyy universitet i Institut fizicheskoy
khimii AN SSSR. Submitted October 28, 1964.

L 36184-66 EWT(m)

SOURCE CODE: UR/0076/66/040/003/0574/0579

ACC NR: AP6010745

AUTHOR: Peshev, O.; Vol'kenshteyn, F. F.

ORG: Moscow State University im. M. V. Lomonosov (Moskovskiy gosudarstvennyy universitet); Institute of Physical Chemistry, Academy of Sciences, SSSR (Institut fizicheskoy khimii Akademii nauk SSSR)

TITLE: Certain irreversible processes in chemisorption¹ on semiconductors

SOURCE: Zhurnal fizicheskoy khimii, v. 40, no. 3, 1966, 571-579

TOPIC TAGS: chemisorption, desorption, semiconductor carrier, adsorption

ABSTRACT: The possible nature of the reversible and irreversible forms of chemisorption is considered from the standpoint of the electronic theory (F. F. Vol'kenshteyn, Electronic Theory of Catalysis on Semiconductors, Fizmatgiz, 1960). The discussion is limited to the case of a homogeneous surface and to the adsorption of an acceptor gas whose particles are in two charge states, negative and neutral. The irreversible form of chemisorption may have a dual nature: (1) it may be due to the hindered desorption of particles in the charged state (mechanism of "apparent" irreversibility) and (2) it may result from the presence of a secondary chemical process on the surface of the semiconductor, such as the reaction of the chemisorbate with the impurity coming to the surface from the volume of the semiconductor (mechanism of "true" irreversibility).

UDC: 541.183

Card 1/2

L 36184-66

ACC NR: AP6010745

Criteria are given for distinguishing these two mechanisms experimentally. Orig. art. has: 5 figures.

SUB CODE: 07/ SUBM DATE: 26Dec64/ ORIG REF: 004/ OTH REF: 002

Card

2/2/11/LP

L 26481-66 EWT(1) IJP(e)

ACC NR: AP6013069

SOURCE CODE: UR/0048/66/030/004/0633/0636

AUTHOR: Sokolov, V.A.; Vol'kenshteyn, F.F.; Brik, O.G.; Kondratenko, M.B. 30

ORG: None L

TITLE: Concerning the role of radical-recombination processes in candoluminescence
/Report, Fourteenth Conference on Luminescence held in Riga 16-23 September 1965/

SOURCE: AN SSSR. Izvestiya. Seriya fizicheskaya, v. 30, no. 4, 1966, 633-636

TOPIC TAGS: recombination luminescence, chemiluminescence, candoluminescence

ABSTRACT: Although candoluminescence - luminescence under the influence of a flame - has been questioned for many years, the authors assert that the existence of this phenomenon has definitely been proved. The mechanism of candoluminescence was hypothetically developed by one of the authors (F.F.Vol'kenshtein, Elektronnaya teoriya kataliza na poluprovodnikakh, Fizmatgiz, Moscow 1960) on the basis of the electronic theory of catalysis and chemisorption on semiconductors and has been discussed and described in other publications by F.F.Vol'kenshtein et al. According to this mechanism excitation occurs at the expense of the energy released incident to recombination of free atoms and radicals in the flame on the surface of the phosphor. In the present paper there are adduced the inferences based on the radical-recombination theory as regards the influence of extraneous gaseous impurities on the intensity of cando-

Card 1/2 2

L 26481-66

ACC NR: AP6013069

luminescence and there are described the results of attempts at experimental verification of the predictions. The inert gas employed in the main experiments was nitrogen and the phosphor was $\text{ZnS} \cdot \text{CdS} : \text{Cu}$. A figure gives curves characterizing the variation of the luminescence intensity of the phosphor with the nitrogen concentration at different temperatures. Another figures shows analogous curves characterizing the influence of CO and O_2 . Comparative experiments to evaluate the recombination coefficient were carried out with non-luminescing CuO . On the basis of general analysis of the data it is concluded that radical-recombination processes play a significant role in excitation of low-temperature luminescence (which, it is asserted, is true luminescence according to the Vavilov-Wiedemann criterion) but also in excitation of high-temperature candoluminescence, which is a special form of equilibrium emission that is not true luminescence. Orig. art. has: 2 formulas and 3 figures.

SUB CODE: 20/

SUBM DATE: 00/

ORIG REF: 007/

OTH REF: 001

Card 2/2

7B

CA VOL'KENSHTEYN, M. V.

3

Raman spectrum of tetraethylammonium iodide. Ya. K. Suirkin and M. V. Volkenstein. *Acta Physicochim. U. R. S. S. 2*, 203-7 (1935) (in German). --A comparison of the data of S. and W. on Et_4NI with previous data on EtI and Et_3N indicates that in Et_4NI the characteristic intense frequencies of EtI , as 497 cm^{-1} assigned to the C-I bond, are absent, and that the I is bound to neither C nor N but is held ionically outside the coordination sphere. New frequencies, especially 607 and 1231 cm^{-1} lead to interpreting the Et_4N ion as a regular tetrahedron with the N atom in the center. V. H. Rathmann

Raman effect of fluosilicic acid. Ya. K. Suirkin and M. V. Volkenstein. *Acta Physicochim. U. R. S. S. 2*, 308-12 (1935) (in German). --Fluosilicic acid (27%) from paraffin bottle was freed of colloidal paraffin (indicated by Tyndall effect), by ultrafiltration through a collodion membrane on a compressed Jena-glass filter. Only one Raman line, $\nu = 649 \pm 5 \text{ cm}^{-1}$, was observed. The SiF_6 ion is interpreted as being octahedral with the Si atom in the center and the Si-F distance 1.93 \AA . The calcd. value for the Raman line is then 640 cm^{-1} . V. H. R.

BC

A-1

Spectroscopic investigation of molecular association. M. V. Kozlovskii. (Acta Physicochim. U.R.S.S., 1968, 4, 367-384).—The influence of mol. association on mol. symmetry as deduced from infra-red and Raman spectra is discussed. If the association forces are weak, corresponding with energies $> 10 \text{ kJ/mol}$, the mole can be regarded as unassociated but having their symmetry distorted. If association energy approaches that of homo- or hetero-polar linking, the product is intermediate between a chemical compound and a van der Waals complex. The existence of a frequency band at 622 cm^{-1} in the Raman spectrum of AcOH and its weakening with dilution is attributed to the association of two AcOH mole.

O. R. H.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

BC a-1

PROCESS AND PROPERTIES INDEX

Raman effect in solutions in [liquid] ammonia.
 I. M. V. YUL'KOVICH (Acta Physicochim. U.R.S.S.,
 1936, 8, 627-644; cf. A., 1936, 137, 1449).
 Raman spectra of solutions of NH_4NO_3 , NH_4CNS ,
 NH_4NO_2 , NH_4CNS , and AgCl in liquid NH_3
 have been measured. Frequencies due to liquid
 NH_3 differ from those observed with the gas. Lines
 characteristic of NO_2 and CNS , but not NH_4 , were
 observed. The absence of NH_4 frequencies is
 explained as due to the formation of $[\text{H}(\text{NH}_4)]$.
 F. I. VI

ASSOCIATE METALLURGICAL LITERATURE CLASSIFICATION

GROUPS 1-2 3-4 5-6 7-8 9-10 11-12 13-14 15-16 17-18 19-20 21-22 23-24 25-26 27-28 29-30 31-32 33-34 35-36 37-38 39-40 41-42 43-44 45-46 47-48 49-50 51-52 53-54 55-56 57-58 59-60 61-62 63-64 65-66 67-68 69-70 71-72 73-74 75-76 77-78 79-80 81-82 83-84 85-86 87-88 89-90 91-92 93-94 95-96 97-98 99-100

Vibrations of polyatomic molecules and their investigation with the help of group theory. M. V. Vol'kenshteyn. *Dokl. Akad. Nauk* 16, 320 (1960). Theoretical and review. Normal vibrations and vibration spectra are classified on the basis of group-theory conceptions. Laws of symmetry and selection are obtained and applied to some specific cases. Exptl. data on the absorption spectra of PCl_5 , PH_3 , *cis*- and *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ and of acetic acid are given. F. H. Rathmann

ca

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Raman effect in binary mixtures with liquid sulfur dioxide. M. V. Vol'kenshtein. *Acta Physicochim. U. R. S. S. 7*, 313-14(1937); cf. *C. A.* 31, 6969².—A mixt. of 3 mols. SO_2 to 2 mols. $(\text{CH}_3)_2\text{O}$ was photographed at room temp. in a sealed tube. The SO_2 frequencies were displaced; the $(\text{CH}_3)_2\text{O}$ frequencies were displaced. unchanged; the $(\text{CH}_3)_2\text{O}$ frequencies were displaced. pure $(\text{CH}_3)_2\text{O}$: 2988, 2947, 2908, 2868, 2813, 1448, 1095, 920, 498; mixt.: 2990, 2952, 2910, 2864, 2821, 1453, 1088, 1008, 411. Pure SO_2 : 1336, 1144, 624.5; mixture: 1335, 1145, 623. Victor Deitz

Raman spectra of solutions of mercuric cyanide in ammonia and pyridine. M. V. Vol'kenshtein. *Acta Physicochim. U. R. S. S. 7*, 315-16(1937).—The Raman spectra of the following solns. are reported: (I) satd. soln. corresponding to $\text{Hg}(\text{CN})_2 \cdot 6\text{NH}_3$, (II) dil. soln. corresponding to $\text{Hg}(\text{CN})_2 \cdot 23\text{NH}_3$, (III) satd. soln. in pyridine. The spectra are: I, 2164; II, 2163; III, 209, 2160 cm^{-1} . The solvent frequencies are unchanged.

VOIKENSHTEIN, M.V.
RAMAN EFFECT AND INTERMOLECULAR INTER-
ACTIONS. (Raman-effekt i Mezhdmolekularnoe
Yzaimodelstvie). M. V. Vol'kenshtein. Translated by
G. Belkov from Uspokhi Fiz. Nauk 18: 163-202(1937).
60p. (TT-499) 25

1ST AND 2ND GROUPS										3RD AND 4TH GROUPS									
PROCESSES AND PROPERTIES INDEX																			
<p>BC</p> <p>Raman spectra of pyrene compounds. M. V. VOLKANSKY and J. K. SIKIN (J. Phys. Chem. Russ., 1958, 12, 677-679).—Dimethylpyrene, its hydrochloride and hydrobromide, coumarin and its hydrochloride, coumarone, and xanthone were investigated. J. J. H.</p>																			
ASD-SEA METALLURGICAL LITERATURE CLASSIFICATION																			
1ST AND 2ND GROUPS										3RD AND 4TH GROUPS									
1ST AND 2ND GROUPS										3RD AND 4TH GROUPS									

Raman effect of hydrocarbons and the analysis of liquid fuels. M. V. Vol'kenshtein. *Uspekhi Khim.* 8, 970-97 (1939). Data are given on the Raman spectra of numerous hydrocarbons and the qual. and approx. quant. analysis of motor fuels by means of their Raman spectra are discussed for various fractions. A complete analysis is possible in solns. F. H. Rathmann

Karpov Inst. Phys. Chem. - Moscow -

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1ST AND 2ND ORDERS																									
PROCESSES AND PROPERTIES INDEX																									
<p><i>BC</i></p> <p><i>Karlov Phys. Chem. Inst.</i></p> <p><i>CA: 33-7664/6</i></p> <p><i>A-1</i></p> <p>Raman effect of pyrone compounds and electronic resonance. M. V. VOLKOVSKAYA and J. K. SIKKIN (Acta Physicochim. U.R.S.S., 1939, 10, 677-700). -The Raman spectra of 2,6-dimethylpyrone (I), coumarin (II), xanthone, coumarone, and dioxan, and oxonium compounds of (I) with HCl and HBr and of (II) with HCl have been investigated. The addition of a H halide produces no considerable effect on the spectrum of (I), thus indicating that there is no O⁺ in these oxonium compounds. The Raman spectrum of (II) resembles those of C₁₀H₈ and coumarone. The effect of electronic resonance on the Raman spectrum is discussed with particular reference to the CO group. The oxonium bond is a result of intermol. interaction stabilised by the presence of a resonance state in the form of the H bond. The dipole moments of (I) and xanthone are calc. from the frequencies of oscillation of the CO group, which are < normal in these compounds. A. J. M.</p>																									
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Raman effect of pyrone compounds and electronic resonance effects. M. V. Vol'kenshchik and Ya. K. Serkin. *J. Phys. Chem.* (U. S. S. R.) 13, 618 (1959). Expt. data are given on the Raman spectra of dimethylpyrone, xanthone, coumarone and dioxane alone and in HCl and HBr solns. The results are considered from the standpoint of Pauling's theory of electron resonance. F. H. Rathmann

V-1615, 3 Jan 52

Karpov Phys. Chem. Inst.

CA: 34-4664/8

ASB-5LA METALLURGICAL LITERATURE CLASSIFICATION

12041 510-03104

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103000-117 000 100

103000-117 000 100

ANALYSIS OF GASOLINES BY MEANS OF THEIR RAMAN SPECTRA.
H. M. V. Volskenskaya and Pt. P. Shurygin. J. Phys. Chem. (U. S. S. R.) 15, 1512-22(1950); cf. C. A. 54, 25815. — V. and S. collect data on the Raman frequencies of a large no. of possible constituents, satd. and unsatd., straight- and branched-chain, cyclic and aromatic, of various types of gasolines. On the basis of exptl. data, they show that the method of Raman spectra applied to various fractions permits of a rapid and sufficiently accurate detn. of the qual. and semiquant. compn. of gasoline fractions boiling up to 100°. The analysis of higher-boiling fractions is more difficult and must in most cases be limited to group rather than to individual-component analysis.
P. H. Rathmann

U-1615, 3 Jan 52

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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200

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Analysis of gasolines by means of Raman spectra. M. V. Val'kenshtein, P. P. Shoyvga and N. N. Shomova. Zhurnal Fiz. Khim. 45, 1040, 1971. 1 p. 1. 35, 005.


The chief problems of Raman spectra in the analysis of motor fuels are reviewed and data are tabulated on the basis for individual compds. In (1) 4 fractions of Syntol gasoline, (2) 10 fractions of Gromy gasoline and (3) gasoline obtained by cracking with $AlCl_3$. Results of the last case lead to the following preliminary conclusions regarding cracking with $AlCl_3$. As a result of the reaction there are formed isoparaffins with 1 side branch and with 1 Me group in the side branch. In all the cases under investigation it was not possible to identify multibranched isoparaffins. The octane no. should drop with increasing b. p. of the fraction. The high octane no. of the lightest fractions is dependent on their large content of isopentane. The content of naphthenes and aromatic compds. is dependent on the selection of the crude oil and the type of process (preliminary purification with H_2SO_4). Nine references. B. Z. Kamich

CA: 35-1608/9

Kaykov Inst. Phys. Chem.

ASB 35A METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS										3RD AND 4TH ORDERS									
PROCESSES AND PROPERTIES INDEX																			
<p>CA</p> <p>The modern theory of natural optical activity. I. M. V. Vol'kenshtein. <i>Uspehi Khim.</i> 9, 1080-1123 (1940).—Review and theoretical, covering the work of Fresnel and Drude, the foundations of the theory of polarization, Herz's and Kuhn's theories, and circular dichroism. Exptl. data for various compds. are compared with the values predicted by these theories. II. Quantum mechanics of optical activity, <i>Ibid.</i> 1263-79.—Theoretical and math. review of the work of Kuhn, Rosenfeld, Kirkwood, and the one-electron model. The superposition of optical activity of sugars, abs. configuration of optically active mole., intermol. forces and optical activity are considered together with the related biochem. problems.</p> <p>F. H. Rathmann</p> <p>2</p>																			
ASB-6LA METALLURGICAL LITERATURE CLASSIFICATION																			
SUBJECTS										SUBJECTS									
SUBJECTS										SUBJECTS									


VOL'KENShteIN, M. V.

PRILEZHAYEVA, E. N., SYRKIN, Ya. K. and VOL'KENShteIN, M. V.
(Karpov Inst. Physical Chemistry, Moscow; State Univ., Minsk)
Acta Physicochim. URSS 12, 176-80 (1940) - in English
The Raman spectra of halogenated ethylenes. Preliminary note.

CA: 34-5756/5

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The Raman effect of oxonium compounds. A. R. Gantmacher, M. V. Vol'kenshtein and Ya. K. Sytkin. *Acta Physicochimica U. R. S. S. 12, 790 (1946)* (in Russian). *cf. C. A. 33, 7064*; 34, 4061. — From expl. English: *cf. C. A. 33, 7064*; 34, 4061. — From expl. data on the Raman spectra for the system $(CH_3)_2O + n HCl$ with $n = 1, 2, 3$ at temps. from -80 to $+20^\circ C$. V. and S. find that interaction causes a lowering of the valence frequency of the C-O-C system, an increase of that of CH_3 , and of the deformation frequency of C-O-C. For 1:1 mixts. the displacement of the CH_3 and C-O-C frequencies is const. throughout the temp. range studied. With increasing amts. of HCl, a new line $\Delta\nu = 500 cm^{-1}$ and a diffuse band at $2400 cm^{-1}$ due to HCl deformed and 14% relative to liquid HCl, appear simultaneously. The 2400 band is attributed to the oxonium resonance complex $CH_3-O^+ \cdots H-Cl^- \cdots HCl$ and the 500 line to a hindered HCl rotation. The evidence indicates trivalent rather than quadrivalent oxygen; the latter is also unlikely from thermodynamical considerations. F. H. R.

CA: 35-976/8

Karpov Phys. Chem. Inst.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

VOL'KENShteIN, M. V.

SHORYGIN, F. F. and VOL'KENShteIN, M. V.
(Karpov Inst. Phys. Chem., Moscow)

CA: 37-2305/6

Bull. acad. sci. URSS, Ser. phys. 1941, 174-81 - English summary
Analysis of benzines by the Raman spectra.